LiFeAs Pnictide Superconductor – a Simple Electrochemical Method of Preparation

M. Kanuchova, M. Majoros, J. Kanuch, Y. Ding, M. A. Susner, M. D. Sumption and E. W. Collings

Abstract—**Unlike the known isoelectronic undoped intrinsic FeAs compounds, LiFeAs does not show any spin-density wave behavior but exhibits superconductivity at ambient pressures without chemical doping. It has a superconducting transition temperature, T_c , of 18 K with electron-like carriers and a very high 0 K upper critical magnetic field, $B_{c2}(0)$, of greater than 80 T making the compound suitable for many high magnetic field applications at cryogenic temperatures. Oxypnictide materials are known for a complexity of their methods of preparation. The reported methods of LiFeAs preparation are based on the solid-state reaction at high temperatures (740-1050 °C) for long times (24 – 60 hours). In the present work a simple electrochemical route is proposed for the preparation of a pnictide LiFeAs superconductor. During electrolysis Li ions in the electrolyte become inserted into the FeAs lattice to form LiFeAs on the surface of the FeAs electrode. The proposed method differs from the existing electrochemical method and also from the traditional high temperature solid-state reaction methods. It is promising for the preparation of LiFeAs bulks and large scale LiFeAs films or tapes for various electric power or high magnetic field applications at cryogenic temperatures.**

***Index Terms*—Oxypnictides, superconductors, LiFeAs, electrolysis**

I. Introduction

LiFeAs crystallizes in the tetragonal PbFCl type unit cell (P4/nmm) with a = 3.7914 Å and c = 6.364 Å. The Fe_2As_2 charge-carrying layers are alternatively stacked along the c-axis with nominal double layers of Li ions [1]. Unlike the known isoelectronic undoped intrinsic FeAs compounds, LiFeAs does not show any spin-density wave behavior but exhibits superconductivity at ambient pressure without chemical doping [1]. It has a superconducting transition temperature, T_c , of 18 K with electron-like carriers and a very high 0 K upper critical magnetic field, $B_{c2}(0)$, of greater than 80 T [1], [2], [3], [4] making the compound suitable for many high magnetic field applications at cryogenic temperatures. The superconducting behavior of LiFeAs (the formal charge balance $Li^{1+}Fe^{2+}As^{3-}$) can be roughly explained by assuming incomplete charge transfer from the strongly polarizing Li atoms to the electron-rich $(Fe_2As_2)^{2-}$ layers. However, this would lead to a hole-like behavior of the carriers, which is in conflict with the thermoelectric power data [1]. The inconsistency may arise from changes in the conduction bands of the FeAs layers due to variations in inter-layer distances. LiFeAs at ambient physical pressure may reside in the equivalent high-pressure state of other undoped iron pnictides due to the chemically induced lattice contraction. This would be consistent with the missing spin density wave state, the observed superconductivity at relatively high T_c, as well as with the negative linear pressure shift of T_c [2].

Oxypnictide materials are known for a complexity of their methods of preparation [5]. The reported methods of LiFeAs preparation are based on the solid-state reaction at high temperatures (740 - 1050°C) for long times (24 – 60 hours) [1], [3], [4], [5]. As reported by Chen [6], advantage may be taken of the small atomic radius of Li to enable an electrochemical method to be used to insert Li into the precursor FeAs to form LiFeAs at room temperature. In the previously reported method [6] an electrode (the cathode) was formed by painting a gelatenous mixture of powdered FeAs and acetylene black dissolved in N-methyl-pyrrolidone (NMP) onto a clean Cu foil which was then heated at 60°C to fully drive off the NMP. The electrode was then placed under pressure to densify the surface layer of FeAs. Once the desired densification was achieved the electrode was dried in a vacuum oven at 120°C for 2 hours before cooling it slowly down to room temperature. The electrode was then punched into a disk shape 8 mm in diameter suitable for use as the cathode in an electrolytic cell. The anode was a lithium film attached to the bottom of the electrolytic cell [6]. The electrolyte was a liquid mixture of ethyl carbonate, diethyl carbonate, lithium hexafluorophosphate, and ethyl methyl carbonate in equal amounts by volume. The use of a closed cell ensured protection of the FeAs electrode from moisture, oxygen, and nitrogen in air.

In this work we present a simple electrochemical method of LiFeAs preparation by electrolysis in an open air from molten LiCl electrolyte (melting point = 605°C) with an inert electrode (e.g. graphite or stainless steel) as the anode and with FeAs pellet as the cathode [7].

II. Electrochemical Method

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A schematic diagram of the electrochemical method is shown in Fig. 1.

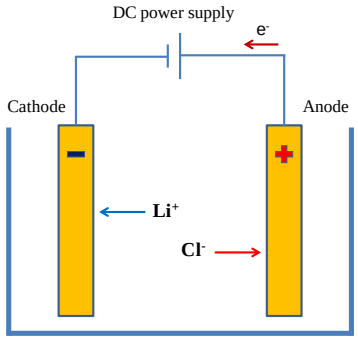


Fig. 1: Schematics of the electrochemical method of LiFeAs preparation from molten LiCl electrolyte in open air (cathode – FeAs pellet, anode - an inert electrode, e.g. stainless steel or graphite).

An FeAs pellet (7 mm in diameter and 2 mm in thickness) served as the cathode electrode. It was prepared by the following method. Fe and As powders (Alfa Aesar, >99.99%) with the mole ratio of 1:1 were mixed thoroughly using a mortar and pestle. The mixture was pressed into a pellet and sintered in an evacuated quartz tube at 500°C for 10 h and then at 750°C for 10 h. The ramp rates used during the heat treatments were 1 °C/min. To obtain a good homogeneity, the obtained pellet was ground into a powder, mixed, and pressed into a pellet again. The final pellet was sintered in an evacuated quartz tube at 750 °C for 10 h. The phase purity of the final pellets was confirmed by XRD powder difractometry using a Scintag XDS 2000 with Cu k_α radiation (λ = 1.5418 Å). The peak positions agreed well with the FeAs data taken from the literature.

Even though the whole electrochemical process could have been done on an open fire on a bench top, a top-loading crucible furnace was used to control the temperature of the electrolyte more precisely. High purity LiCl (99.9%, ultra dry) was used as the electrolyte. The operation temperature was set to 610°C, which is slightly above the melting point of LiCl at ambient pressure (605°C). The electrochemical process was performed at a voltage of 6 V provided by a dc power supply which worked in a regime of a constant voltage source. The current was < 0.2 A during the process.

III. Results and Discussion

In electrolysis or electroplating, sufficient voltage should be provided by the power supply. The voltage-current relationship follows Ohm's law. The voltage E_{cell} (in Volts) between the electrodes of an electrochemical cell is given by the Nernst equation [8]

$$E_{cell} = E^0_{cell} - \frac{RT}{nF}\ln(Q) \qquad (1)$$

where E^0_{cell} is the voltage of the electrochemical cell under standard conditions (pressure of 1 atmosphere and temperature of 25°C), T is the temperature in degrees of Kelvin, R is the gas constant (8.31441 J/mol-K), F is the Faraday constant (96484.6 C/mol), n is the valence change, Q is the reaction quotient. For a reaction (reactants on the left side, products on the right side) given by eq. (2)

$$aA + bB \Leftrightarrow cC + dD \qquad (2)$$

the reaction quotient has the form

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b} \qquad (3)$$

where [C] is the molar concentration of the product C etc.
The standard voltage of the electrochemical cell E^0_{cell} can be estimated by the following way. Consider an idealized cell for the electrolysis of molten LiCl with a pair of inert electrodes (Fig. 1). Because the LiCl salt has been heated above its melting point, the Li^+ ions flow toward the negative electrode (cathode) and the Cl^- ions flow toward the positive electrode (anode). When Li^+ ions collide with the negative electrode, the power supply provides a large enough potential to force these ions to pick up electrons to form a lithium metal. Cl^- ions, which collide with the positive electrode are oxidized to Cl_2 gas, which bubbles off at this electrode. The net effect of passing an electric current through the molten LiCl salt is to decompose lithium chloride into its elements, lithium metal and chlorine gas. We then have the following two half reactions:

Cathode (-): $Li^+(l)+e^- \rightarrow Li(s)$
Anode (+): $2Cl^-(l) \rightarrow Cl_2(g)+2e^-$

which result in an overall reaction

$$2LiCl\ (l) \rightarrow 2Li\ (s) + Cl_2\ (g) \qquad (4)$$

From a table of standard potentials we get that the potential needed to reduce Li^+ ions to lithium metal is -3.04 V (the so called standard reduction potential $E^0_{reduction}$). The equation for the anode is reversed, so the sign of the standard potential must be reversed. It follows that the potential required to oxidize Cl^- ions to Cl_2 is -1.36 V (the so called standard oxidation potential $E^0_{oxidation}$). Then $E^0_{cell} = E^0_{reduction} + E^0_{oxidation}$ = -3.04 -1.36 = -4.4 V. Here $E^0_{cell} < 0$ which means the reaction is not spontaneous.

The voltage of the cell E_{cell} under the non-standard conditions (T=610° C) can be calculated using eq. (1). In our case the eq. (2) has the form

$$LiCl \Leftrightarrow Li^+ + Cl^- \qquad (5)$$

Here we have 1 mole of LiCl , i.e. [A] = 1 in eq. (2). Similarly on the right hand side of (5) we have 1 mole of Li^+ and 1 mole of Cl^-, i.e. [C] = [D] = 1 in eq. (2). The relative content of these elements does not change as the reaction proceeds. This gives Q = {[C][D]}/[A] = 1, which means that $E_{cell} = E^0_{cell}$ (eq. (1)), i.e. the minimum required voltage for our electrochemical reaction is 4.4 V.

However, the voltage U of a real electrochemical cell is much more complex. The cell voltage U is the entire voltage applied to an electrochemical cell. The cell voltmeter shows this value which is measured from the entrance to the exit of the cell busbar system and this is the voltage which the power source (or a battery) must provide. It consists of a bath voltage U_{bath} and of an entry-bath and exit-bath voltage. The entry-bath (U_{entry}) and exit-bath (U_{exit}) voltage is basically a voltage drop along the electrodes and the current leads attached to the

power supply or the battery (Fig. 1). The bath voltage U_{bath} is the voltage between the electrodes inside the electrolyte (Fig. 1), i.e. it is the ohmic resistance of the electrolyte. It has the following components (Fig. 2): E_{cell} – minimum voltage necessary for electrolysis, U_{bub} – bubble voltage due to an increased resistance of the electrolyte caused by gas production on anode, U_{AC} – anodic concentration overvoltage necessary to overcome the concentration gradient of the reacting species at the anode, U_{AR} - anodic reaction overvoltage applied to make the reaction at the anode proceed with an appropriate speed, U_{CC} – cathodic concentration overvoltage necessary to overcome the concentration gradient of the reacting species at the cathode. Then

$$U_{bath} = E_{cell} + U_{bub} + U_{AC} + U_{AR} + U_{CC} \quad (6)$$

Then the cell voltage U is given by the following equation

$$U = U_{entry} + U_{exit} + U_{bath} \quad (7)$$

Our experiments showed that a cell voltage U = 6 V is sufficient to run the electrolysis of molten LiCl in our electrochemical cell with a reasonable speed.

The intercalation of lithium into FeAs can be described by the following chemical reaction

$$Li^+ + (FeAs)^- \rightarrow LiFeAs$$

The actual reaction mechanism might be more complicated than this due to a phase transition of FeAs to LiFeAs. This process might be similar to intercalation of lithium ions into graphite electrodes (see e.g. [9]) which receives much attention in the battery community because of its practical applications to rechargeable lithium batteries. In this case the reaction mechanism is complicated by the phase transition related to the staging phenomenon of the graphite intercalation compound. Also in [6] it was observed that LiFeAs was produced mainly in the first cycle even though the Li ions can be electrochemically extracted and re-incalated.

A stereo microscope top-view of the pellet prepared by the present method is shown in Fig. 3a; Fig. 3b shows its cross section. Its center is unreacted FeAs, which is in turn surrounded by LiFeAs layer. An excess Li compounds surround the surface of the pellet. This is confirmed by powder XRD analysis (Fig. 4) which shows a multiphase sample. Because LiFeAs is quite new, its XRD spectra are not available from the database.

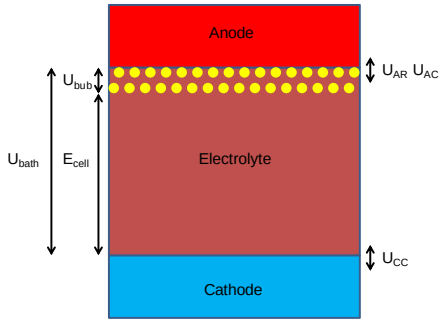
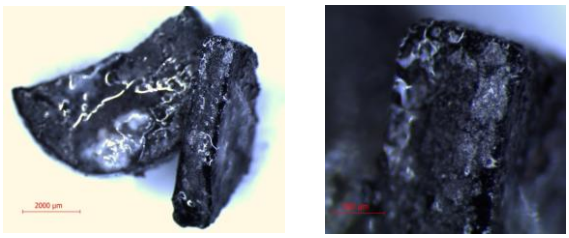


Fig. 2: Components of the bath voltage U_{bath}.

We used single crystal XRD data published in [1] as a reference of LiFeAs material. X-ray analysis, which typically takes about 12 hours for fine structural analysis, is complicated by the fact that LiFeAs pnictide samples degrade when exposed to humidity and oxygen from the air. As a result, apart from traces of the LiFeAs phase and unreacted FeAs in Fig. 4 we also observed peaks which can be identified with LiOH, Li_2O_2, Li_2O, Fe_3O_4 and $FeAsO_4$. The fast degradation of the sample is probably triggered by a high reactivity of the excess Li with oxygen and moisture in the air. The wide peak in Fig. 4 around 14 degrees may be a result of the sample surface being rough.



a) b)

Fig. 3: a) A stereo microscope cross-section of the FeAs pellet with a LiFeAs layer on its surface, b) a magnified view of the pellet cross-section.

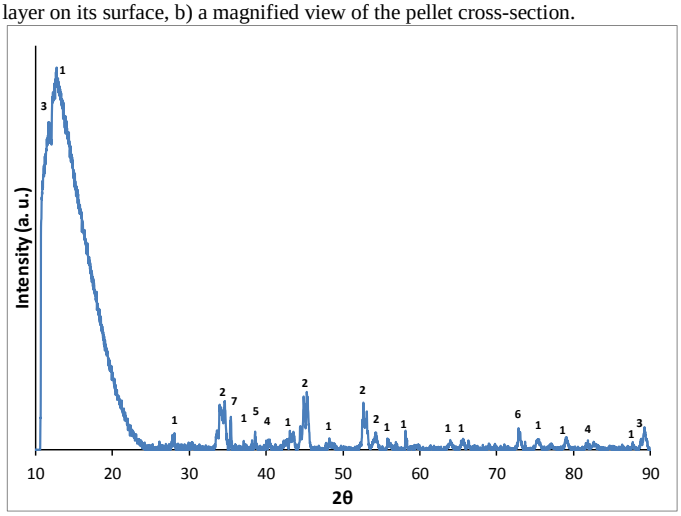


Fig. 4: Powder XRD of the LiFeAs sample prepared by the electrolysis as described in the text (1 – LiFeAs, 2 – FeAs, 3 – Li_2O_2, 4 – LiOH, 5 – Li_2O, 6 – Fe_3O_4, 7 – $FeAsO_4$).

The LiFeAs layers prepared in the present work were further characterized by magnetic measurements using a Quantum Design Model 6000 PPMS VSM magnetometer, a dc extraction magnetometer, by ac susceptometry and by resistance measurements in different magnetic fields at different temperatures. The magnetic moment of a sample plotted against temperature in an applied magnetic field of 100 Oe is shown in Fig. 5a, with the estimated T_c = 17 K. Qualitatively the same dependence as reported in [6] was obtained, apart from a slightly higher T_c obtained for our sample. This analysis proves superconductivity in LiFeAs. The measured magnetic moment of the LiFeAs film is affected by a large superimposed ferromagnetic moment of unreacted FeAs in the sample. Data corrected for this ferromagnetic background are shown in Fig. 5b. In-phase (M') and out-of-phase (M'') magnetic moment of a part of the LiFeAs pellet is shown in Fig. 6. The M'' moment shows a peak below 10 K which is a characteristic sign of type-II superconductors. On the same piece of sample a DC magnetic moment in heating and cooling at H_a = 100 Oe followed by zero-field warming was measured. The results are shown in Fig. 7. After turning the magnetic field off the magnetic moment decreases as the temperature increases due to induced supercurrents (green

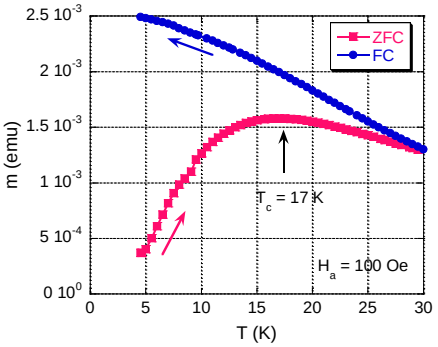


Fig. 5a: DC magnetic moment vs. temperature of the LiFeAs film measured in zero-field-cooled (ZFC) and field-cooled (FC) regimes. Estimated T_c = 17 K. The magnetic moment of LiFeAs material is affected by a superimposed ferromagnetic moment of unreacted FeAs in the sample.

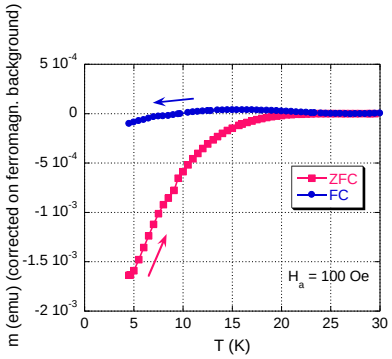


Fig. 5b: Magnetic moment vs. temperature of the LiFeAs film, corrected on ferromagnetic background due to unreacted FeAs in the sample. Estimated T_c = 17 K.

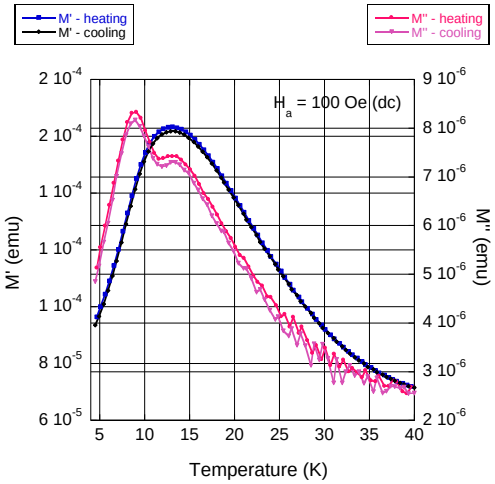


Fig. 6: AC magnetic moment (*M'* and *M''*) vs. temperature in heating and cooling at 100 Oe applied dc magnetic field (a different piece of the same pellet as shown in Fig. 5). Estimated T_c = 15 K.

diamonds). The estimated T_c of this sample piece is about 15 K. Resistive measurements (Fig. 8) indicate a change in resistance at about 20 K. The fact that the resistance does not go to zero indicates an inhomogeneity of LiFeAs material in the pellet. A work toward optimizing the preparation process is in progress.

IV. Conclusion

A successful preparation of LiFeAs film using a simple electrochemical method has been presented. The method is simple and easy to employ. Unlike the previous procedure [6] it does not need a Li anode and it works in open air, which makes it suitable for practical applications. Given the fact that B_{c2} of this material is about 80 T at 4.2 K makes it attractive for high magnetic field applications. A further improvement of the method is possible [7]. The work is in progress.

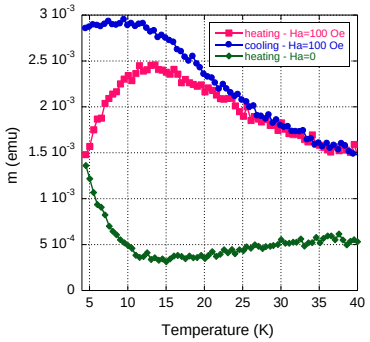


Fig. 7: DC magnetic moment in heating and cooling at H_a = 100 Oe followed by zero-field warming (diamonds – green) (the same sample piece as in Fig. 6).

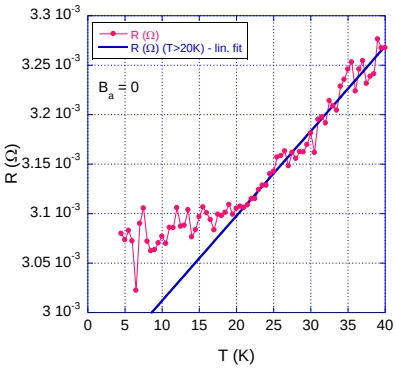


Fig. 8: *R(T)* dependence in cooling at zero applied magnetic field (the same piece of pellet as in Fig. 5).

References

[1] J. H. Tapp, Z .Tang, B. Lv, K. Sasmal, B. Lorentz, P. C. W .Chu and A. M .Guloy ,"LiFeAs: An intrinsic FeAs-based superconductor with Tc=18 K," *Phys. Rev. B* ,vol.78, pp 060505, 2008.

[2] M. Gooh, B. Lv, K .Sasmal, J. H. Tapp, Z .J. Tang, A. M. Guloy, B. Lorenz and C. W. Chu, "Superconductivity in ternary iron pnictides: AFe2As2 (A = alkali metal) and LiFeAs," *Physica C* , vol. 470, pp S276-S279, 2010.

[3] X.C. Wang, Q.Q. Liu, L.X. Yang, Y.X. Lv, W.B. Gao, S.J. Zhang, R.C. Yu, C.Q. Jin," Superconductivity of ''1 1 1"-type iron arsenide compounds," *Physica C,* vol. 470, pp S307 – S308, 2010.

[4] Y.J. Song, J. S. Ghim, B. H. Min, Y. S. Kwon,M. H. Jung, and J.S.Rhyee, "Synthesis, anisotropy and superconducting properties of LiFeAs single crystal," Appl. Phys. Lett.,vol.96, pp 212508, 2010.

[5] M. Majoros, M .Kanuchova, M. A. Susner, M .D. Sumption, C. S. Myers, S .D. Bohnenstiehl, and E. W. Collings ," *IEEE Trans. Appl. Supercond.,"* vol.21, pp 2853, 2011.

[6] N. Chen, S. Qu, Y. Li, Y. Liu, R. Zhang, and H. Zhao," Synthesis of LiFeAs superconductor by electrochemistry at room temperature," *J. Appl. Phys.*, Vol.107, pp 09E123, 2010.

[7] M.Majoros, M .Kanuchova, M .D. Sumption, E. W. Collings, *patent pending* ,2012.

[8] A. J. Bard, L. R. Faulkner, " Electrochemical Methods – Fundamentals and Applications," John Wiley & Sons, Inc. 1980.

[9] T. Piao, S-M. Park, C-H. Doh, and S-I. Moon, "Intercalation of Lithium Ions into Graphite Electrodes Studied by AC Impedance Measurements," *J. Electrochem. Soc* , vol.146, pp 2794 – 2798, 1999.